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Description

This invention relates to a method of producing a semiconductor device equipped with electrodes and interconnections consisting of tungsten or molybdenum.

As is known well in the art, polycrystalline silicon has been used widely as a material for electrodes and interconnections of a semiconductor device.

Polycrystalline silicon has been used for the following reasons. In order to miniaturize an MIS transistor, it is inevitable to employ so-called "self-alignment" techniques which form source and drain by ion implantation using the gate electrode as the mask. After ion-implantation is completed, however, annealing at high temperatures must be made by all means to remove damage of the source and drain region that has developed due to ion-implantation.

Accordingly, to produce a miniature MOS transistor by self-alignment, the gate electrode must be made of a material which can withstand the heat-treatment at high temperatures, and polycrystalline silicon having a high melting point has replaced aluminum that was used widely and previously.

The disadvantage of this polycrystalline silicon is, however, that its electric resistance is greater than that of metals. Since higher integration and miniaturization of semiconductor devices has made a rapid progress in recent years, the width of the electrode or interconnection becomes extremely small. Accordingly, if polycrystalline silicon is used, the resistance of the electrode or interconnection does not become sufficiently low and it is difficult to produce a miniature semiconductor device having high characteristics.

To solve this problem, the use of tungsten or molybdenum has been proposed in place of polycrystalline silicon so as to form electrodes and interconnections. Since tungsten or molybdenum have a high melting point, they can withstand annealing at high temperatures and moreover, since their electric resistance is far lower than that of polycrystalline silicon, the problem described above, that occurs when polycrystalline silicon is used, does not develop even when the width of the electrode or interconnection is extremely small.

However, tungsten and molybdenum have the problem that they are more easily oxidized than silicon. When heat-treatment is carried out at about 300 °C or above in an oxidizing atmosphere, therefore, they are rapidly oxidized, disclosed or peeled off from the substrate.

An insulating film (SiO_2 film) deposited on a semiconductor substrate is damaged or contaminated if an ion-implantation is effected using the gate as the mask to form the source and drain during the fabrication of an MOS transistor. Accordingly, the damaged or contaminated insulating film must be removed by etching after completion of gate formation and ion-implantation and the heat-treatment is carried out in an oxidizing atmosphere to re-grow an SiO_2 film on the semiconductor substrate. This process is carried out generally and widely and is an indispensable step to form a high reliability MOS transistor. (This process or treatment will be hereinafter referred to as "light oxidation").

When polycristalline silicon is used for the gate electrode and the interconnections, the light oxidation described above can be carried out smoothly without any problems. However, when tungsten or molybdenum is used, the gate electrode and interconnections are highly oxidized because tungsten and molybdenum are extremely oxidizable. Therefore, such semiconductors having high reliability and a high integration density cannot be produced.

In the "Technical Digest of the International Electron Devices Meeting", December 1982, pages 564 to 567, a selective SiO_2 layer formation on a Mo electrode is disclosed. It is described that by annealing a poly-Si/MoO_2/Mo structure in an H_2 atmosphere the inside of the poly-Si film is oxidized into SiO_2 by oxygen generated in a MoO_2 reduction.This process is called "Internal Oxidation" because it is restricted to the internal reaction between the MoO_2 layer and the overlaying poly-Si.

To eliminate the problems with the prior art described above, the present invention is directed to provide a method of producing a semiconductor device in which electrodes and interconnections are formed by using tungsten or molybdenum without any problems.

That is, the present invention is directed to provide a method of producing a semiconductor device in which silicon is oxidized selectively without substantially oxidizing tungsten or molybdenum.

To accomplish the object given above, in the method according to the invention as described in attached claim 1, there is selectively oxidized silicone alone without substantially oxidizing tungsten or molybdenum by carrying out heat-treatment in a mixed atmosphere of hydrogen and water vapor.

<u>Brief description of the drawings:</u>

Figure 1 is a diagram showing the preferred ranges of vapor-hydrogen partial pressure ratio and heating temperature;

Figure 2 is a diagram showing the relation between the water temperature of a bubbler and the partial pressure ratio in the resulting hydrogen;
Figure 3 is a diagram showing the relation between the partial pressure ratio in hydrogen and the thickness of the resulting SiO_2 film;
Figures 4 and 5 are diagrams showing the relation between the thickness of the resulting SiO_2 film and the heating time and between the thickness of the SiO_2 film and the heating temperature, respectively; and
Figures 6 through 11 are process diagrams showing other embodiments of the present invention, respectively.

Description of preferred embodiments:

As is well known, Si and most metals form their oxides upon reacting with water vapor.

According to the examination carried out by the inventor of the present invention, however, it has been found that only Si can be selectively oxidized without the oxidation of W and/or Mo by heating Si and W and/or Mo in a mixed atmosphere consisting of the vapor and hydrogen.

Though the mechanism of this reaction has not been clarified fully, it is assumed that even if W and Mo are oxidized by the vapor to their oxides, the resulting oxides are immediately reduced to the metallic state by the coexisting hydrogen, whereas Si is not reduced by hydrogen but remains as-oxidized by the vapor.

It has also been found out that the selective reduction of W and Mo is significantly affected by the partial pressure ratio

$$P_{H_2O}/P_{H_2}$$

(which will be hereinafter represented by R).

In other words, the relation represented by curves a, b and c in Figure 1 has been found existing between the partial pressure ratio R_c, when the reduction of W, Mo and Si oxides starts, and various temperatures.

As can be seen clearly from Figure 1, all of W, Mo and Si are reduced in the region below the curve c representing the reduction of SiO_2 but if the heat-treatment is carried out inside the region between the curve representing the reduction of WO_3 and the curve c described above, only Si can be selectively oxidized without substantially oxidizing W.

Similarly, only Si can be oxidized selectively without substantially oxidizing W and Mo if the heat-treatment is carried out in the region interposed between the curve b representing the reduction of MoO_2 and the curve c described above.

When the heat-treating temperature is 1,000°C, for example, only Si can be selectively oxidized without oxidizing W and Mo (with the oxides being reduced), if R is in the range of from 10^{-6} to about 1.

If the present invention is applied to the "light oxidation" when fabricating MOS transistors, for example, the SiO_2 film can be formed on the Si substrate without oxidizing the electrodes and interconnections made of W or Mo, and the present invention is extremely advantageous for the fabrication of the MOS transistors having high integration density.

If the heat-treating temperature is below about 400°C, however, the oxidation speed of Si becomes extremely slow and when it is above about 1,200°C, on the other hand, deformation of the diffusion region formed in the substrate becomes so remarkable and damage of the reaction tube becomes also great. For these reasons, the heat-treating temperature is selected in the range of from about 400 to about 1,200°C.

Example 1

After an SiO_2 film was formed on a silicon wafer by a known thermal oxidation process, a 0.3 μm-thick W or Mo film was formed by sputtering on the SiO_2 film and was then heat-treated at 1,000°C for 30 minutes in an N_2 or Ar atmosphere containing 1 ppm of oxygen as an impurity.

According to the procedures described above, the W and Mo films were not mostly oxidized but there were also the cases in which only the film edge portions were oxidized or the entire surface of the film was oxidized, so that a stable result could not be obtained. Incidentally, the Si surface was oxidized in all cases.

Next, the sample described above was heated at 1,000°C for 30 minutes in the hydrogen/vapor atmosphere in which the partial pressure ratio R of vapor to hydrogen was changed stepwise from 1, 3 x

10^{-1}, 3×10^{-2}, ..., 1×10^{-6} so as to examine the state of oxidation of W, Mo and Si. As a result, oxidation of W and Mo was observed when R was 1 but could not be observed when R was below 3×10^{-1}. On the other hand, Si was oxidized in all cases. Here, the state of oxidation was examined by X-ray photoelectronic spectrometry.

Table 1

vapor / material	H_2/H_2O					N_2	A_r
	R (partial pressure ratio of H_2/H_2O)					O_2 · 1 ppm	
	1	3×10^{-1}	3×10^{-2}	1×10^{-4}	1×10^{-6}		
Si	X	X	X	X	X	X	X
W	X	O	O	O	O	X	X
Mo	X		O		O	X	X

Remarks: X .... oxidized

O .... not oxidized

Example 2

This example illustrates the relation between the oxidation of Si and the partial pressure ratio R

$$(P_{H_2O}/P_{H_2})$$

of H_2O and H_2 the atmosphere when heating is effected in the H_2/H_2O atmosphere.

The vapor-containing hydrogen could be obtained by passing hydrogen through a bubbler containing pure water, and the vapor quantity in hydrogen could be adjusted to a desired value by changing the temperature of the pure water in the bubbler.

Thus, heat-treatment was carried out at 950 °C for 10 minutes by changing the ratio R

$$(P_{H_2O}/P_{H_2})$$

and the thickness of the SiO_2 film formed on the silicon wafer was measured using an ellipsometer.

The silicon wafer used for the measurement was washed by hydrofluoric acid before heating to remove in advance the oxide film on the wafer surface. The result obtained was shown in Figure 3. The thickness of the SiO_2 film increased substantially proportionally to the value R within the range of $O < R \leqq 0.4$. Figure 4 shows the result of the measurement of time dependence of the thickness of the SiO_2 film when the heating temperature was 1,000 °C and R was 0.05. Similarly, Figure 5 shows the dependence of the thickness of the SiO_2 film upon the heating temperature when R was 0.05.

Example 3

This example illustrates the application of the present invention to the fabrication of an MOS field effect transistor.

First, as shown in Figure 6a, a tungsten film 1 and a silicon dioxide film 2' were formed sequentially in thickness of 350 nm and 60 nm, respectively, on a 20 nm-thick silicon dioxide film 2 that was formed on the

surface of a silicon substrate 3. The silicon dioxide film 2' and the tungsten film 1 were then patterned sequentially into the pattern of a gate electrode by known dry etching techniques. Next, an impurity ion was implanted into the silicon substrate 3 through the silicon dioxide film 2 using the electrode consisting of the silicon dioxide film 2' and the tungsten film 1 as the mask, to form a source and drain 4 as shown in Figure 6b. The silicon oxide films 2, 2' at the portions other than the portion covered with the W film 1 were selectively removed using a hydrofluoric acid solution diluted to 1/10 by water, as shown in Figure 6c.

Next, the heat-treatment was effected at 900 °C for 15 minutes in hydrogen containing 5% of vapor to grow an about 10 nm-thick silicon dioxide film 2'' on the exposed silicon substrate 3 as shown in Figure 6d. Thereafter, a phosphoglass layer 5 was deposited in a thickness of about 500 nm over the entire surface and contact holes were bored by photoetching. Aluminum interconnections 6 were formed to complete the MOS transistor as shown in Figure 6e.

This example corresponds to the light oxidation step in the silicon gate process, and the tungsten gate transistor produced by this step exhibited the improvement in the MOS characteristics (break-down voltage of the SiO_2 film and variance of breakdown voltage).

Example 4

A 350 nm-thick tungsten film 1 was deposited and patterned on a 20 nm-thick SiO_2 film 2 that was formed on a Si single crystal substrate 3 as shown in Figure 7a. Heat-treatment was effected at 1,000 °C for one hour in hydrogen passed through a bubbler of pure water (hydrogen containing about 3% of water), whereby the thickness d_1 of the SiO_2 film 2 of the portion covered with the tungsten film 1 and the thickness d_2 at the portion not covered with the tungsten film 1 increased to 30 nm and 70 nm, respectively. However, the tungsten fim 1 was not oxidized. The moisture content in hydrogen, heating temperature and heating time were increased (or decreased) in accordance with Example 2 and the thickness d_1 and d_2 of the SiO_2 film increased (or decreased) in response to the former. After the heat-treatment, the breakdown voltage of the SiO_2 film was measured using the tungsten film as the electrode. The breakdown voltage was found increased than before the heat-treatment. It was thus confirmed that the present invention could effectively prevent degradation of the characteristics of the SiO_2 film due to the heat-treatment.

Example 5

A 300 nm-thick tungsten film 1 was vacuum deposited on a 20 nm-thick SiO_2 film 2 that was formed on an Si crystal substrate 3 as shown in Figure 8a, and an 80 nm-thick SiO_2 film 2' was deposited by CVD on the tungsten film 1. Unnecessary portions were removed by sequentially etching the SiO_2 film 2' and the tungsten film 1. The sample was then heated at 900 to 1,000 °C for 15 minutes in hydrogen containing 3 to 20% of water, whereby the portion of the SiO_2 film 2''' not covered with the tungsten film 1 became thicker in the same way as in Example 4 but the thickness of the SiO_2 film 2 below the tungsten film 1 remained substantially unaltered, as shown in Figure 8b. As can be understood from this Example, when those materials (at least one of polycrystalline Si, PSG, SiO_2, Si_3N_4 and the like) which are generally used as a mask for the diffusion of an impurity are used for the heat-treatment on the tungsten film, the function of the mask for the prevention of oxidation can be more improved than when heat-treatment is carried out using the tungsten film alone.

Example 6

A 350 nm-thick molybdenum film 8 was vacuum deposited on a polycrystalline silicon substrate 7 as shown in Figure 9a and unnecessary portions were removed by etching the film 8. The sample was heat-treated at 900 °C for 30 minutes in hydrogen containing 5% of vapor. As a result, the molybdenum film 8 reacted with the polycrystalline silicon substrate 7 and a molybdenum silicide layer 9 was formed at their contact portion. On the other hand, the portion of the surface of the polycrystalline silicon substrate 7 at which the molybdenum film 8 did not exist and which was exposed was oxidized to form a thick SiO_2 film 2. According to this method, contact could be established between the molybdenum film and the polycrystalline silicon substrate and at the same time, an insulating film could be formed on the polycrystalline silicon in self-alignment with the molybdenum electrode. Substantially the same result could be obtained by use of a tungsten film in place of the molybdenum film.

Example 7

Figures 10a through 10c illustrate another method of producing an MOS field effect semiconductor device to which the present invention is applied.

First, as shown in Figure 10a, an about 350 nm-thick tungsten film was formed on a 20 nm-thick field insulating film (SiO_2 film) 2 (reference numeral 2''' represents a field silicon diode film formed in advance) that was formed on the surface of an Si crystal substrate 3. The tungsten film was then patterned to form a gate electrode 1. Next, the sample was heated in an oxygen atmosphere of about 400°C to form an about 50 nm-thick tungsten oxide film 10 on the surface of the tungsten film 1 as shown in Figure 10b. Using the tungsten oxide film 10 and the tungsten film 1 as the mask, an impurity was doped to the surface region of the Si substrate 3 and the sample was heat-treated at 950°C for 30 minutes in hydrogen containing 5% of vapor, thereby forming source and drain region 4. In this process, the tungsten oxide film 10 on the surface of the tungsten film 1 served as the mask for doping the impurity by ion implantation or the like, and was reduced to tungsten due to the subsequent heat-treatment in the H_2O-H_2 atmosphere, as shown in Figure 10c. Due to the heat-treatment described above, the silicon oxide film on the source-drain region 4 became thicker than the oxide film below the gate electrode.

Example 8

An about 250 nm-thick molybdenum silicide film 9 was formed on the surface of a 300 nm-thick polycrystalline silicon plate 7 as shown in Figure 11a and a molybdenum film 8 was vacuum deposited on it in a thickness of about 300 nm. Unnecessary portions were removed by etching to form an electrode 8. The sample was heated at 900°C for 10 minutes in hydrogen containing 5% of water, whereby a part of the molybdenum electrode 8 was converted to its silicide, and an SiO_2 film 2 was formed on the exposed surface of the resulting molybdenum silicide film 9. The reason was assumed to the fact that the portion below the molybdenum electrode was converted to the silicide due to the supply of Si from the polycrystalline silicon film 7 as the base to the molybdenum silicide film 9 and the SiO_2 film could be formed at the exposed portion of the molybdenum silicide film. As can be understood clearly from this example, the present invention makes it possible to grow the SiO_2 film not only on Si but also on the silicide film.

When tungsten silicide was used in place of molybdenum silicide, the exposed surface of tungsten silicide could also be oxidized without oxidizing molybdenum and tungsten.

The same result could be obtained when silicides of molybdenum and tungsten were formed on single crystal silicon in place of polycrystalline silicon.

Example 9

Next, still another method of producing an MOS field effect semiconductor device in accordance with the present invention will be described with reference to Figure 6 which shows Example 3.

A 350 nm-thick tungsten film 1 was deposited on a 20 nm-thick gate SiO_2 film 2 that was formed on an Si crystal substrate 3. When etching the sample to a gate electrode pattern, there had been conventionally the problem that the SiO_2 film around the gate electrode was also damaged so that the SiO_2 film became thinner by about 10 nm and the breakdown voltage of the gate SiO_2 film got deteriorated. When the sample was heated at 900°C for 10 minutes in hydrogen containing 3% of water after etching the gate electrode of tungsten in accordance with the present invention, however, the damage of the SiO_2 film was recovered and at the same time, a fresh SiO_2 film grew. Accordingly, the breakdown voltage of the gate SiO_2 film was improved. This heat-treatment may be effected after etching and removing the SiO_2 film around the gate, and the same result could be obtained when the heat-treatment was effected without removing the SiO_2 film.

Example 10

The following two kinds of wafers were prepared. First, an Si wafer having formed a tungsten film on the surface thereof was heated in an oxygen atmosphere to form a 300 nm-thick tungsten oxide film. Separately, an Si wafer was washed by hydrofluoric acid to prepare a wafer (up to 2 nm thick) hardly having any oxide film. These two kinds of wafers were heated at 1,000°C for 1 hour in hydrogen containing 3% of water and their surfaces were analyzed by X-ray photoelectronic spectrometry. As a result, the tungsten oxide was reduced to tungsten due to the heat-treatment but the Si wafers were oxidized and an SiO_2 film was formed on the surface. The resulting SiO_2 film was found to be 58 nm thick as a result of measurement by an elipsometer.

As described above, silicon can be selectively oxidized without oxidizing tungsten and molybdenum during the fabrication of a semiconductor device by using H_2O/H_2 as the atmosphere of heat-treatment and by adjusting their partial pressure ratio. As a result, the so-called "light oxidation" process, that has been employed in the conventional polycrystalline silicon gate process, can be also used in the fabrication process of MOS transistors using tungsten or molybdenum for the gate. In other words, the present invention eliminates the problem of oxidation of tungsten and molybdenum during fabrication of semiconductor devices and a process approximate to the one used in the conventional polycrystalline silicon process can now be used. Moreover, the characteristics of the resulting device can be remarkably stabilized in comparison with the tungsten or molybdenum gate process not using the H_2O/H_2 heat-treatment.

Example 11

In an Si gate process for fabricating an MOS transistor using a polycrystalline silicon film for a gate electrode, a so-called "glass flow" process is effected in which after the Si gate is covered with a PSG (phosphosilicate glass) which is an inter-layer insulating film, the surface of the PSG film is made smooth. When Mo or W is used for the gate, however, the oxidation of Mo or W due to oxygen will occur when heated in oxygen or nitrogen, even if Mo or W is covered with the PSG film because pin holes exist in the PSG film. When the sample was heated at 1,000 °C for 30 minutes, for example, in the $H_2 + H_2O$ (5% moisture content) atmosphere in accordance with the present invention, however, the surface of the 500 nm-thick PSG film (P concentration = 12 mol%) covering W was made sufficiently flat. Accordingly, the present invention made it possible to carry out "glass flow" without the possibility of oxidation of W or Mo.

As described above, the present invention makes it possible to selectively oxidize only Si and to form an SiO_2 film without oxidizing W or Mo and to remarkably improve the reliability and producibility of semiconductor devices using these materials. Particularly when W or Mo is used as the low resistance electrode of an MOS field effect semiconductor device, compatibility with the Si gate process can be improved. For instance, the "light oxidation" process becomes feasible. Since the present invention uses hydrogen containing water as the heating atmosphere, it can be easily practised using an ordinary heating apparatus consisting of a silica tube and an electric furnace and is excellent in both mass-producibility and economy.

Claims

1. A method of producing a semiconductor device comprising:
   forming a tungsten or molybdenum film (1) of a desired shape on a silicon substrate (7), on an SiO_2 film (2) disposed on a silicon substrate (3) or on a tungsten or molybdenum silicide film (9); and
   heating the resulting structure in a hydrogen atmosphere containing water vapor, the partial pressure ratio between the water vapor and the hydrogen gas and the heat treating temperature being selected as values falling in the range between the curve a and the curve c of Figure 1 for a tungsten film or falling in the range between the curve b and the curve c of Figure 1 for a molybdenum film, so as to selectively oxidize the surface of said silicon substrate or silicide film without oxidizing surfaces of said tungsten or molybdenum film.

2. The method according to claim 1, wherein the heat treatment temperature is in the range from about 400 °C to about 1200 °C.

3. The method according to claim 1, wherein said silicon substrate is a single crystal silicon substrate (3) or a polycrystalline silicon substrate (7).

4. The method of producing a semiconductor device according to claim 1, including the steps of
   forming an SiO_2 film (2) on said silicon substrate (3);
   forming said tungsten or molybdenum film (1) in the desired shape on said SiO_2 film;
   doping an impurity having a conductivity type opposite to that of said silicon substrate (3) to the surface region of said silicon substrate using said tungsten or molybdenum film (1) as a mask; and
   carrying out said heat treatment.

5. The method according to claim 4, wherein doping of said impurity is carried out by laminating a mask film (2') consisting of at least one member of a phosphosilicate glass film, an SiO_2 film and an Si_3N_4 film on said tungsten or molybdenum film (1) and then effecting ion implantation.

6. The method according to claim 4, wherein said tungsten or molybdenum film (1) is the gate electrode of an MIS field effect semiconductor device.

7. The method according to claim 4, wherein said heat-treatment is carried out after a portion of said SiO_2 film (2) where said tungsten or molybdenum film (1) ist not deposited is removed by etching.

Revendications

1. Procédé pour fabriquer un dispositif à semiconducteurs comprenant :
   la formation d'une pellicule de tungstène ou de molybdène (1) possédant une forme désirée sur un substrat en silicium (7), sur une pellicule (2) de SiO_2 disposée sur un substrat en silicium (3) ou sur une pellicule de siliciure de tungstène ou de molybdène (9) ; et
   le chauffage de la structure résultante dans une atmosphère d'hydrogène contenant de la vapeur d'eau, le rapport entre les pressions partielles de la vapeur d'eau et du gaz hydrogène et la température de traitement thermique étant choisis en tant que valeurs entrant dans la zone comprise entre la courbe a et la courbe c de la figure 1 pour une pellicule de tungstène ou entrant dans la zone comprise entre la courbe b et la courbe c de la figure 1 pour une pellicule de molybdène, de manière à oxyder sélectivement la surface dudit substrat en silicium ou de ladite pellicule de siliciure sans oxyder des surfaces de ladite pellicule de tungstène ou de molybdène.

2. Procédé selon la revendication 1, selon lequel la température de traitement thermique se situe dans la gamme comprise entre environ 400 °C et environ 1200 °C.

3. Procédé selon la revendication 1, selon lequel ledit substrat en silicium est un substrat en monocristal de silicium (3) ou un substrat en silicium polycristallin (7).

4. Procédé pour fabriquer un dispositif à semiconducteurs selon la revendication 1, incluant les étapes comprenant
   la formation d'une pellicule (2) de SiO_2 sur ledit substrat en silicium (3);
   la formation de ladite pellicule de tungstène et de molybdène (1) avec la forme désirée sur ladite pellicule de SiO_2;
   le dopage de la région superficielle dudit substrat en silicium avec une impureté possédant un type de conductivité opposé à celui dudit substrat en silicium (3), moyennant l'utilisation de ladite pellicule de tungstène ou de molybdène (1) en tant que masque; et
   l'exécution dudit traitement thermique.

5. Procédé selon la revendication 4, selon lequel le dopage de ladite impureté est exécuté en déposant une pellicule stratifiée formant masque (2') comprenant au moins un élément incluant une pellicule de verre au phosphosilicate, une pellicule de SiO_2 et une pellicule de Si_3N_4 sur ladite pellicule de tungstène ou de molybdène (1), puis en effectuant une implantation ionique.

6. Procédé selon la revendication 4, selon lequel ladite pellicule de tungstène ou de molybdène (1) est l'électrode de grille d'un dispositif à semiconducteurs à effet de champ MIS.

7. Procédé selon la revendication 4, selon lequel ledit traitement thermique est effectué après l'élimination par attaque chimique d'une partie de ladite pellicule (2) de SiO_2, dans laquelle ladite pellicule de tungstène ou de molybdène (1) n'est pas déposée.

Patentansprüche

1. Verfahren zur Herstellung einer Halbleiteranordnung, wobei
   ein Wolfram- oder Molybdän-Film (1) gewünschter Form auf einem Siliciumsubstrat (7), auf einem auf einem Siliciumsubstrat (3) angeordneten SiO_2-Film (2) oder auf einem Wolfram- oder Molybdänsilicidfilm (9) ausgebildet wird, und
   der sich ergebende Aufbau in einer wasserdampfhaltigen Wasserstoffatmosphäre erwärmt wird, wobei das Partialdruckverhältnis zwischen dem Wasserdampf und dem gasförmigen Wasserstoff sowie die Wärmebehandlungstemperatur mit Werten gewählt werden, die für einen Wolframfilm in den Bereich zwischen der Kurve a und der Kurve c in Figur 1 bzw. für einen Molybdänfilm in den Bereich

zwischen der Kurve b und der Kurve c in Figur 1 fallen, um die Oberfläche des Siliciumsubstrats bzw. Silicidfilms selektiv zu oxidieren, ohne Oberflächen des Wolfram- bzw. Molybdänfilms zu oxidieren.

2. Verfahren nach Anspruch 1, wobei die Wärmebehandlungstemperatur im Bereich von etwa 400 °C bis etwa 1200 °C liegt.

3. Verfahren nach Anspruch 1, wobei das Siliciumsubstrat ein Einkristall-Siliciumsubstrat (3) oder ein polykristallines Siliciumsubstrat (7) ist.

4. Verfahren zur Herstellung einer Halbleiteranordnung nach Anspruch 1, umfassend die folgenden Schritte:
Ausbilden eines SiO_2-Films (2) auf dem Siliciumsubstrat (3),
Ausbilden des Wolfram- bzw. Molybdänfilms (1) in der gewünschten Form auf dem SiO_2-Film,
Dotieren des Oberflächenbereichs des Siliciumsubstrats (3) mit einem Störstoff eines zu dem Siliciumsubstrat entgegengesetzten Leitfähigkeitstyps unter Verwendung des Wolfram- bzw. Molybdänfilms (1) als Maske, und
Durchführen der Wärmebehandlung.

5. Verfahren nach Anspruch 4, wobei die Störstoffdotierung dadurch ausgeführt wird, daß auf den Wolfram- bzw. Molybdänfilm (1) ein Maskenfilm (2'), der aus einem Phosphosilicatglasfilm und/oder einem SiO_2-Film und/oder einem Si_3N_4-Film besteht, aufgeschichtet und anschließend eine Ionenimplantation durchgeführt wird.

6. Verfahren nach Anspruch 4, wobei der Wolfram- bzw. Molybdänfilm (1) die Gate-Elektrode einer MIS-Feldeffekt-Halbleitereinrichtung darstellt.

7. Verfahren nach Anspruch 4, wobei die Wärmebehandlung durchgeführt wird, nachdem ein Teil des SiO_2-Films (2), auf dem der Wolfram- bzw. Molybdänfilm (1) nicht aufgetragen ist, weggeätzt worden ist.

FIG. 1

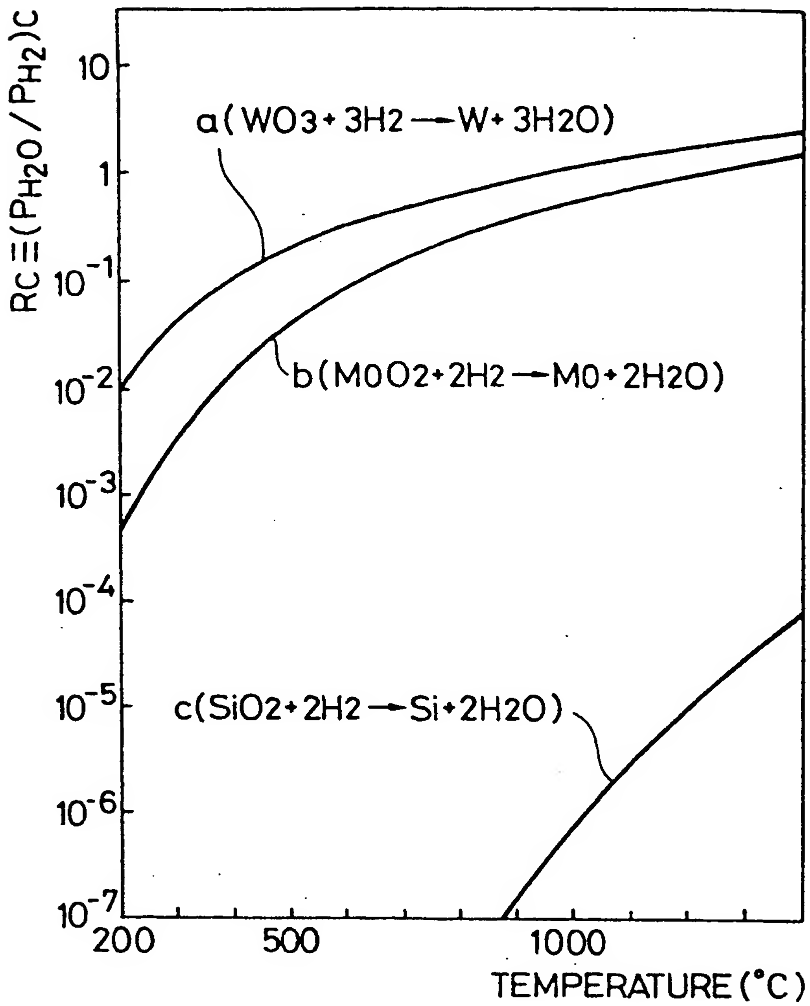

RC ≡ (PH2O / PH2)C
10
1
10-1
10-2
10-3
10-4
10-5
10-6
10-7
a(WO3+3H2→W+3H2O)
b(MOO2+2H2→MO+2H2O)
c(SiO2+2H2→Si+2H2O)
200
500
1000
TEMPERATURE (°C)

FIG. 2

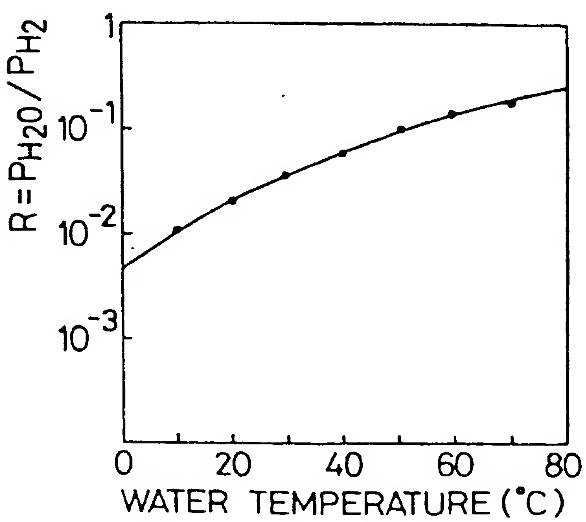

R = PH2O / PH2
1
10-1
10-2
10-3
0
20
40
60
80
WATER TEMPERATURE (°C)

FIG. 3

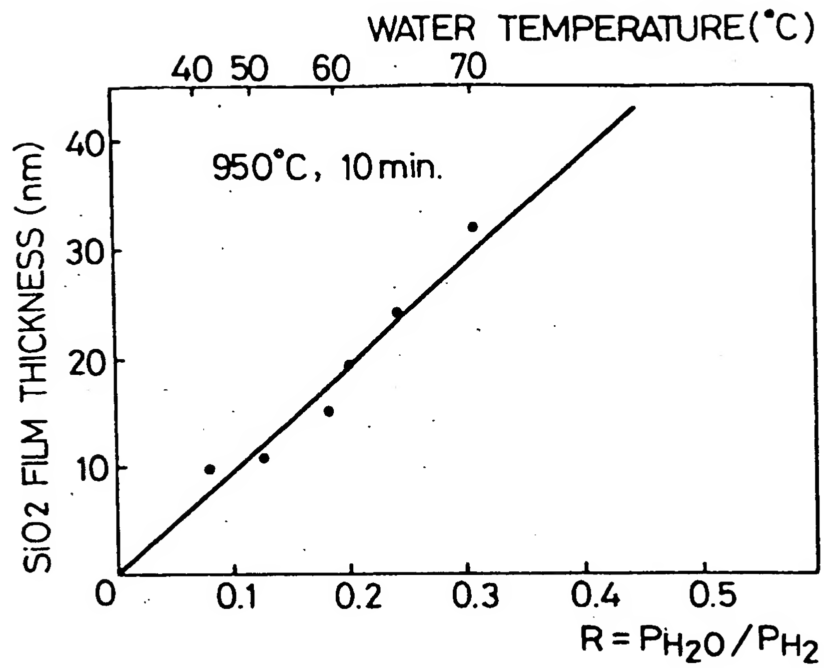

WATER TEMPERATURE(°C)
40 50 60 70
950°C, 10 min.
SiO2 FILM THICKNESS (nm)
40
30
20
10
0
0.1
0.2
0.3
0.4
0.5
R = PH2O / PH2

FIG 4

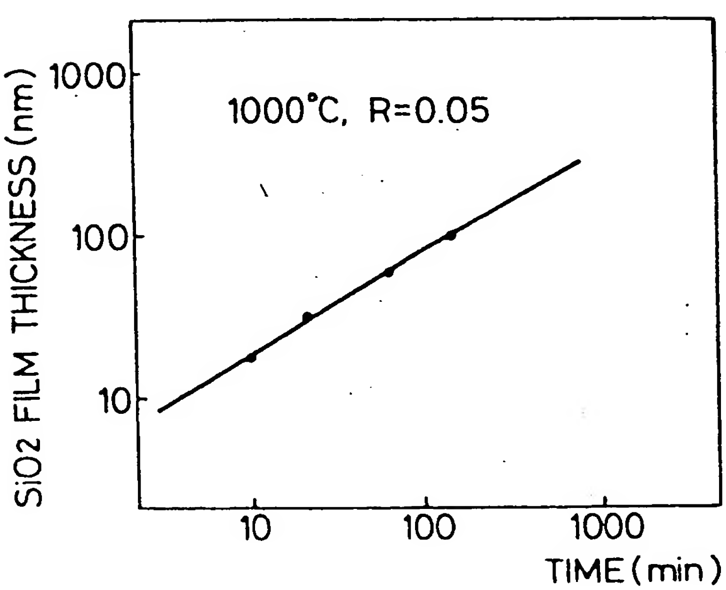

1000°C, R=0.05
SiO2 FILM THICKNESS (nm)
1000
100
10
10
100
1000
TIME (min)

FIG. 6a

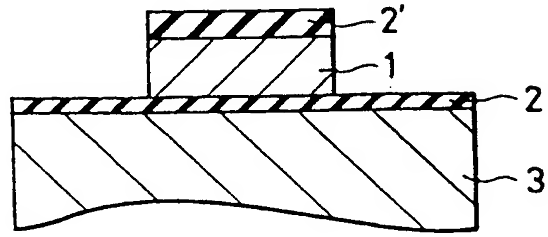


FIG. 6b

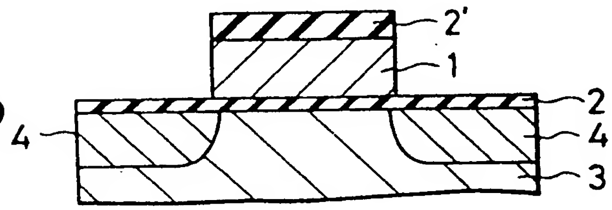


FIG. 6c

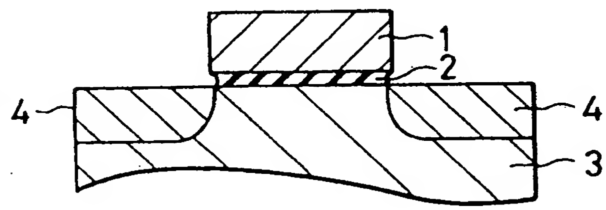


FIG. 6d

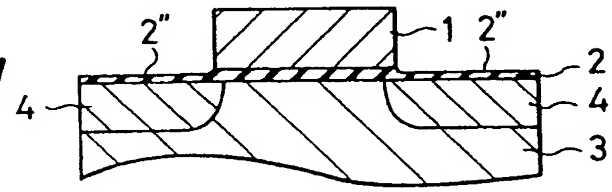


FIG. 6e

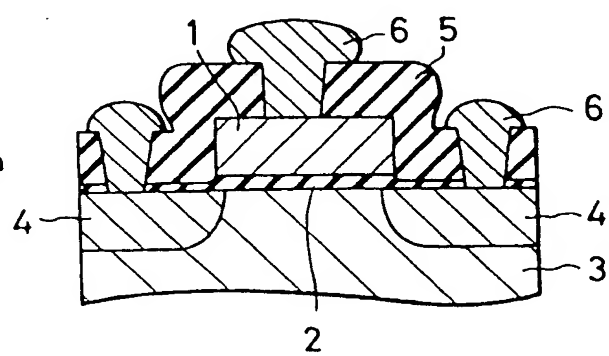


FIG. 5

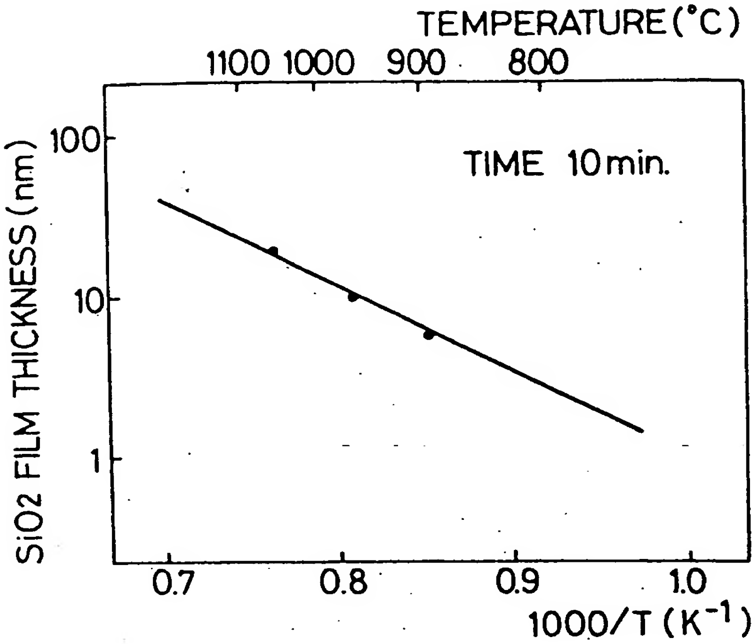


FIG. 7a

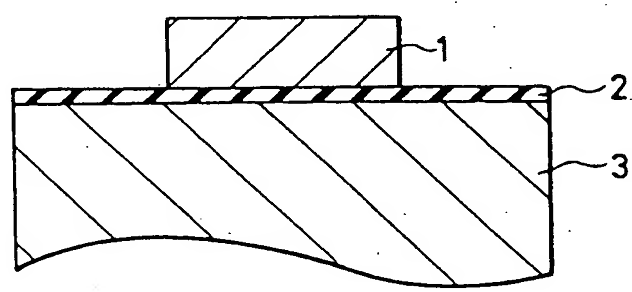


FIG. 7b

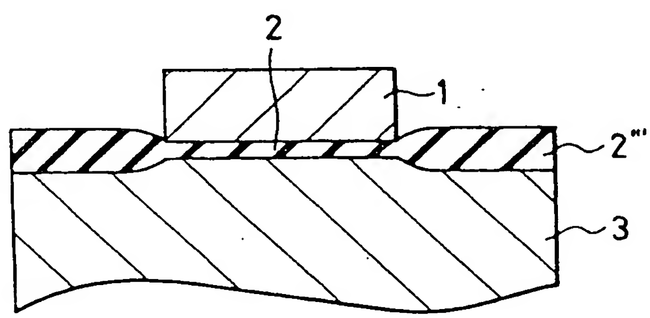


FIG. 8a

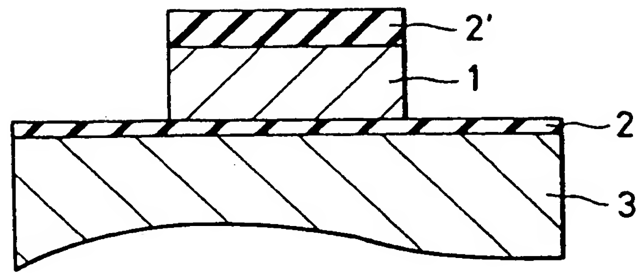


FIG. 8b

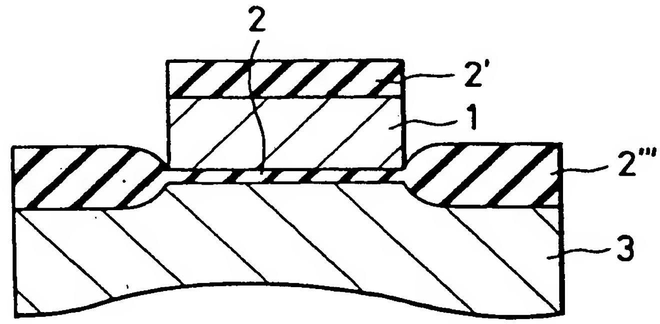


FIG. 9a

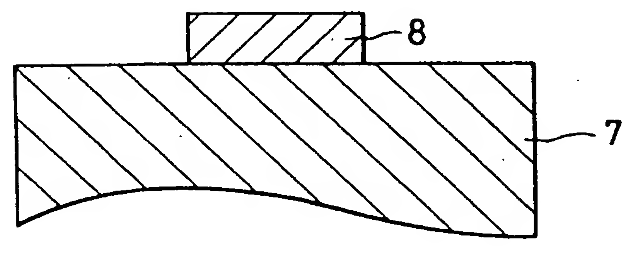


FIG. 9b

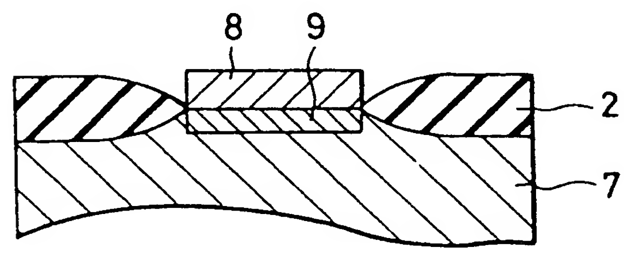


FIG. 10a

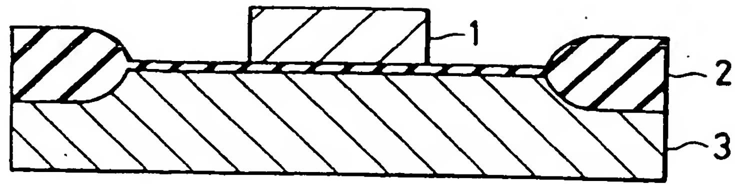


FIG. 10b

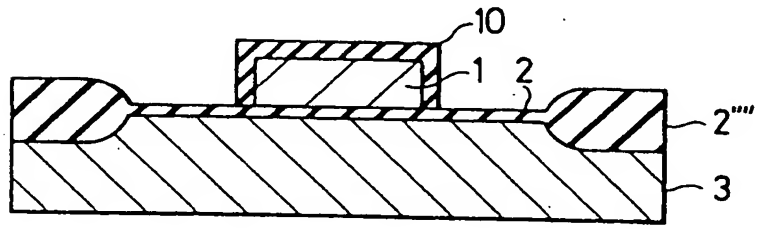


FIG. 10c

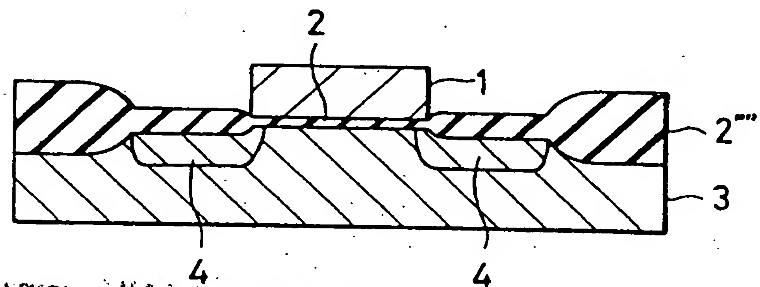


FIG. 11a

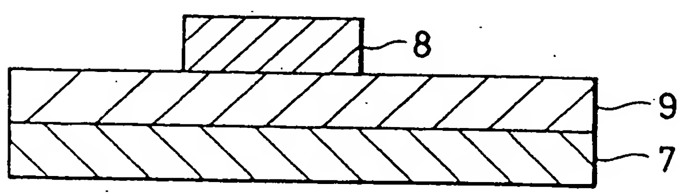
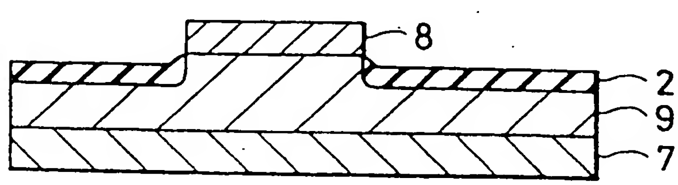


FIG. 11b



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